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(54) A PROCESS FOR THE PREPARATION OF ALIPHATIC POLYCARBONATES WHICH HAVE TERMINAL HYDROXYL GROUPS

(71) We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany of, 509, Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of aliphatic polycarbonates which contain hydroxyl groups. It relates in particular to difunctional aliphatic linear polycarbonates of molecular weight 600 to 5,000 which contain terminal hydroxyl groups and which are suitable for use as raw materials for the production of high grade polyurethane resins.

Aliphatic polycarbonates which are strictly difunctional and which carry terminal hydroxyl groups are of great interest for the synthesis of elastomers by the diisocyanates polyaddition process as these give products which are resistant to hydrolysis. However it has not been possible to make these on a sufficiently large scale because the synthetic methods which are available do not yield sufficiently pure difunctional polycondensation products.

The synthesis of aliphatic polycarbonates has been known for 40 years. The use of diphenylcarbonate as the source of a chain linking CO fragment in the synthesis of polycarbonates is also known. The preparation of aliphatic carbonates can be carried out either in the presence of catalysts and/or, (as in the synthesis of aromatic polycarbonates) in a melt at temperatures above 205° C. (See for example U.S. Patent Specification No. 2,210,817).

These syntheses provided unsatisfactory products which could only be used to a limited extent for the production of high grade polyurethanes. The main disadvantage of aliphatic polycarbonates produced by the known processes is that immediately after the addition of the diisocyanate to the molten aliphatic

polycarbonate the viscosity increases very greatly. This, therefore, results in manipulation difficulties with the NCO prepolymer; other disadvantages are the odours which are present in the molten polycarbonates which are caused by unknown by-products of the polycarbonate synthesis and lastly the unsatisfactory behaviour of polyurethane elastomers produced from polycarbonates when they are subjected to pressure deformation stresses.

UV spectroscopic analysis of aliphatic polycarbonates prepared by the known process showed that these unwanted phenomena can be attributed to many causes, for example to incomplete reaction of phenyl carbonate groups, less than quantitative removal of the phenol liberated, or side reactions which originate either in the diphenylcarbonate or in the aromatic-aliphatic carbonic acid esters formed as intermediate products and which lead to unwanted by-products, such as phenylalkylethers.

The term "total phenol" will be used hereinafter to mean the amount of these interfering by-products. This figure is obtained by adding together the concentrations of bound phenol in phenylalkylether and phenylalkylcarbonate and the amount of residual free phenol. These can be obtained easily and accurately by U.V. spectroscopy. The process known from the literature for producing aliphatic polycarbonates which is carried out at about 200 to 250° C. gives a total "total phenol" of 0.45 to 0.55%, based on C₆H₅OH, which was determined on 15 batches some of which were produced on a large scale (see comparison test 2 in Example 1).

A process has now been found in which by a suitable choice of the reaction conditions aliphatic polycarbonates can be produced with a "total phenol" of only one tenth to one fifth of the value found in similar polycarbonates produced by the conventional processes.

The present invention thus provides a pro-

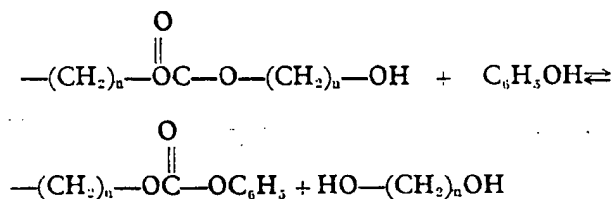
cess for the production of a difunctional aliphatic polycarbonate which has terminal hydroxyl groups and a molecular weight of 600 to 5,000 and a "total phenol", as herein-
 5 defined, of not more than 0.15% by weight, which comprises the steps of reacting at least one dihydric alcohol and diphenylcarbonate
 10 (a) in a first reaction stage at 100 to 170° C. under reduced pressure until more than 90% of the amount of phenol which should theoretically be liberated has distilled off, (b) in a
 15 second reaction stage in which the quantitative reaction of diphenylcarbonate or of intermediate products containing phenyl carbonate groups is then completed under reduced pressure at 170 to 205° C. and (c) if necessary
 20 in a third reaction stage in which the product of the process is freed from residual phenol at 180 to 205° C. under reduced pressure.

In kinetic experiments it was observed that the reaction between a dihydric alcohol and diphenylcarbonate can proceed rapidly at temperatures of only 120 to 170° C. although this
 25 depends to some extent on the purity of the starting materials. If the phenol liberated is continuously removed from the reaction equilibrium by distillation in this temperature range, the formation of by-products is largely
 30 suppressed. The conditions of temperature and pressure in the first stage of polycondensation are therefore chosen to lie about 20 to 50° C. above the corrected boiling point of phenol but at least 5° C. below the corrected boiling
 35 point of the dihydric alcohol. These conditions must be maintained until at least half the theoretically calculated quantity of phenol has been removed. From then onwards, the conditions of temperature and pressure may be
 40 chosen to lie above the corrected boiling point of the dihydric alcohol since the alcohol is by that time present in the form of oligomeric polycarbonate and therefore has only a very small partial vapour pressure. Nevertheless

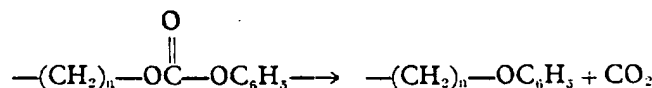
the temperature must not exceed 170° C. until more than 90% of the theoretically calculated quantity of phenol has been distilled
 45 off. The reaction proceeds at a high velocity even under these conditions but no side reactions occur and, in particular, the very undesirable thermal decomposition of phenyl
 50 alkyl carbonate groups into CO₂ and phenyl alkyl ether does not occur. This reaction is irreversible and leads to chain breaking both during the synthesis of the aliphatic polycarbonate and during the subsequent reaction
 55 of the polycarbonates with diisocyanates to form high molecular weight elastomers.

In the known method of producing polycarbonates, the importance of rapid removal of phenol below 170° C. was not sufficiently
 60 recognised. Consequently, owing to the equilibrium between the components, a high static concentration of phenol was allowed to remain in the reaction for far too long at a high temperature, invariably above 200° C., so that
 65 the reaction was artificially slowed down and the formation of by-products was greatly promoted. These conditions led to the high "total phenol" values of 0.45 to 0.55% which cause the formation of malodorous by-products
 70 and promoted the synthesis of polycarbonates which do not have an accurately defined degree of branching.

It was also observed in kinetic investigations that even at 215° C. and 4 mm Hg the residual phenol can only be incompletely removed
 75 from a highly viscous polycarbonate melt. Although the residual phenol content diminishes over the course of several hours at this temperature, the unwanted phenyl alkyl ether content at the same time increases so that the
 80 "total aryl" values remain undesirably high, as shown in comparison test 1 in Example 1. Phenyl alkyl ether is formed from phenol, for example by way of an ester interchange equilibrium as follows:



wherein $n \geq 5$



90 in which the static concentration of aliphatic carbonate lies below the measurable limit of 0.01%.

By the process according to the invention, aliphatic polycarbonates which contain

hydroxyl end groups can be prepared from
 95 diphenylcarbonate and the "total aryl" of these is only 1/10 to 1/5 the value mentioned above. As is well known, dihydric alcohols, for example hexane - 1,6 - diol, react completely

and quantitatively with diphenylcarbonate at temperatures below 190° C. The main reaction is therefore carried out below 170° C. Tertiary amines, cyclic amidines and/or hydroxides, carbonates or phenolates of alkali metals or of alkaline earth metals may be added in concentrations of a few parts per thousand to the reaction mixtures to lower the starting temperature of the reaction in known manner, i.e. to catalyse the liberation of phenol. In all cases, however, the first reaction stage must be carried out below 170° C. In order to react residual diphenylcarbonate or phenylcarbonate end groups quantitatively, the reaction mixture is then heated in a second stage to temperatures of 170° to a maximum of 205° C. preferably under a pressure of less than 15 mm Hg. Although the melt then still contains a large amount of free phenol, the phenyl carbonate concentration rapidly falls towards zero whilst the phenyl alkyl ether content does not rise significantly. In the third stage at 180 to 205° C. under a pressure preferably of not more than 15 mm Hg, the phenol must be removed as quickly as possible from the reaction mixture. Under laboratory conditions, very rapid removal of phenol may be achieved by distillation at 0.1 to 0.5 mm Hg. These conditions, however, cannot be realised in large scale industrial production of aliphatic polycarbonate. Residual phenol can, however, be removed very efficiently even on a large industrial scale in this temperature range by passing a stream of inert gas through the melt. The vacuum must be maintained during this operation. The phenol content is then reduced surprisingly rapidly at, for example, 200° C. under 5 to 30 mm Hg and falls to concentrations of less than 0.1% within a few hours. It is surprising that this method of after-treatment removes even those by-products which cause an unpleasant smell in the melt so that an odourless product is obtained which only contains less than 0.15% by weight of aromatic by-products.

Suitable hydroxyl compounds for the process of the invention are, for example, pentane - 1,5 - diol, hexane - 1,6 - diol, octane - 1,8 - diol, dodecane - 1,12 - diol, methyl- and dimethylpentane - 1,5 - diol, methyl-, dimethyl- and trimethylhexane - 1,6 - diol, hexane - 1,6 - diol - mono- and bis - 2 - hydroxyethylether, hexane - 1,6 - diol - mono- and bis - 5 - hydroxycaproic acid esters, bis-6 - hydroxyhexyl ester of adipic acid, diethylene glycol, tri- and tetra - ethylene glycol, oligomeric polyether of propane - 1,2 - diol having molecular weights of up to 700, 1,4-bis - hydroxymethylcyclohexane, hydroquinone - bis - 2 - hydroxyethylether, 4,4' - bis-2 - hydroxyethoxy - 2,2 - diphenyl propane and 4,4' - bis - 2 - hydroxy - 2,2 - dicyclohexylpropane.

Diphenylcarbonate is used in all cases as the source of CO groups. Nitrogen, helium, hydrogen, methane, ethane, propane, carbon monoxide and, in particular, carbon dioxide have been found to be suitable for use as inert gases. The gases should preferably be free from oxygen because oxygen imparts a dark colour to the aliphatic polycarbonates in the melt. The gas may, if desired, be recycled but must then be passed through a cooler or better still a scrubbing tower to remove volatile by-products.

Aliphatic polycarbonates prepared by this process can conveniently be converted into valuable elastomers, which have an extremely high resistance to hydrolysis, by the diisocyanate polyaddition process.

The following Examples illustrate the invention:—

EXAMPLE 1

Reaction according to the invention.

Hexanediolcarbonate - (1,6) with after-treatment in a stream of CO₂ under vacuum. 47.07 kg of hexane - 1,6 - diol are reacted with 79.02 kg of diphenylcarbonate in a 150 l tank equipped with a stirrer, distillation head and gas inlet system, and the temperature is raised to 155° C. in 6 hours. A vacuum is then applied and the distillation of phenol sets in at a pressure slightly above 100 mm Hg. While the temperature is maintained at 155±2° C., the vacuum is reduced to 25 mm Hg in 24 hours and the temperature is then raised to 200° C. and the vacuum is reduced to 12 mm Hg in the course of a further 10 hours. After another 14 hours' heating at 200° C. and 12 mm Hg, no phenyl carbonate groups can be detected by UV spectroscopy (less than 0.01%) and the bound and free phenol content is 0.39% by weight. A stream of CO₂ is then introduced into melt at such a rate that a vacuum of 18 to 30 mm Hg is maintained, some volatile substance, mainly phenol, being distilled off. The reaction has been quantitatively completed after another 8 hours. The pale yellow, odourless melt solidifies to a waxy hard material which has a melting point of 49 to 52° C. and an OH number of 58.8. As by-products, less than 0.01% by weight of phenylcarbonate end groups, 0.04% by weight of phenol in the form of phenoxy-alkylether derivative and 0.05% by weight of free phenol can be detected by UV spectroscopy ("total phenol" 0.09%).

Comparison test 1:

About 10.0 kg of material is removed from the condensation reaction mixture at the site of the manufacturing process where the amount of phenol present as phenyl carbonate is 0.01 per cent by weight but the total phenol content is still 0.39% by weight, and the material

removed is treated at 200° C. and 4 mm Hg for 10 hours. The amounts of aromatic by-products indicated in column 1 of the table

are obtained in this way, and the amounts of by-products indicated in column 2 are obtained by similar treatment for 20 hours.

	Starting material	Column 1	Column 2
Phenol as phenyl carbonate	0.01%	0.01%	0.01%
Phenol as phenyl alkylether	0.01%	0.06%	0.10%
Phenol	0.39%	0.23%	0.17%
"Total phenol"	0.40%	0.29%	0.27%

10 In spite of the long after-treatment at 200° C. and 4 mm Hg hardly any reduction in the "total phenol" is found.

ether, 0.07% of phenol, i.e. a total of 0.67% of aromatic by-products. The viscosity (80° C.) 1690 cP.

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Comparison test 2:

(Representative of the known manufacturing process)

15 92.3 kg of hexane - 1,6 - diol and 155.3 kg of diphenyl carbonate are heated in a vessel equipped with stirrer with vigorous stirring for 10 hours at 210° C. with continuous removal of phenol which distills off slowly and this temperature is maintained for another 7
20 hours until distillation slows down; phenol yield: 38.0 kg (27% of the theory). The temperature is then reduced to 200° C. and a vacuum is slowly applied. After 16 hours' heating at 200° C. at 150 mm Hg, the tem-
25 perature is increased to 215° C. and the vacuum is reduced to 12 mm Hg until no more distillate is obtained (15 hours). The yield of crude phenol is less than 100% of the theoretical and the solidification point at
30 38.8° C. In order to reduce the residual phenol content, the melt is again after-treated at 215° C. and 8 mm Hg for 20 hours, a dark yellow material of OH number 51.1 being obtained after a reaction time of 68 hours.
35 The "total phenol" obtained is made up as follows: 0.04% of phenol as phenyl carbonate end groups, 0.56% of phenol as phenylalkyl-

EXAMPLE 2
Mixed O - (2 - hydroxyethyl) - hexanediol- (1,6) - hexanediol - (1,6) - polycarbonate with after-treatment in a stream of CO₂ under vacuum.

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34.90 kg of hexane - 1,6 - diol, 15.5 kg of 1,6 - hexanediol - mono - 2 - hydroxyethyl- ether and 77.70 kg of diphenylcarbonate are mixed in a 150 l vessel equipped with stirrer at about 100° C., and then heated at 155±
50 2° C. for 6 hours. By gradual application of a vacuum, the pressure is reduced to 20 mm Hg in the course of 20 hours. During another 10 hours, the temperature is raised to 200° C. and the vacuum increased to about 12 mm Hg
55 and finally the vacuum is increased to about 6mm Hg for a further 14 to 15 hours at 200° C. The pale yellow melt then has an OH number of 50.0. The phenol content in the form of phenylcarbonate is less than 0.01%
60 by weight, and the phenyl ether 0.01% by weight, the free phenol content 0.74% by weight. As an after-treatment, the temperature is maintained at 200° C. and a stream of CO₂ is passed through the melt while the vacuum is maintained at 20 to 30 mm Hg,
65 another 300 to 400 g then distilling off.

OH number 44.8; phenol as phenylcarbonate <0.0%
phenol as phenylalkylether 0.03%
70 phenol 0.07%

EXAMPLE 3

75 Mixed O - (2 - hydroxyethyl) - hexanediol- (1,6) - hexanediol - (1,6) - polycarbonate, prepared in the presence of trimethylolpropane to compensate for the chain breaking by phenoxy end groups.

To compensate for the aromatic content of about 0.080% in the form of monofunctional chain breaking agents, a small quantity of tri-

methanolpropane is added to balance statistically the functionality of the condensation reaction mixture.

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34.90 kg of hexane - 1,6 - diol, 15.15 kg of 1,6 - hexanediol - mono - 2 - hydroxyethyl- ether, 95 g of trimethylolpropane and 77.70 kg of diphenylcarbonate are heated at 155° C. for 6 hours, and the phenol is then substantially removed in the course of 15 hours under

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a vacuum which gradually rises to a final pressure of 25 mm Hg. In the course of a further 15 hours the temperature is raised to 200° C. and the vacuum to 12 mm Hg, and the temperature is maintained at 200° C. for 24 hours. CO₂ is then passed through for 10 hours at 200° C. while a vacuum of 25 to 30 mm Hg is maintained. OH number of the end product 52.7.

10	Phenol as phenylcarbonate	0.01%
	Phenol as phenylalkylether	0.05%
	Phenol content	0.04%

The pale yellow melt is odourless.

EXAMPLE 4

15 Diethylene glycol polycarbonate prepared on laboratory scale and therefore without the inert gas treatment.

In a 10 l three-necked flask equipped with stirrer, immersed thermometer and reflux condenser, 3420 g of diethylene glycol (32.3 mol) and 6098 g of diphenylcarbonate (28.5 mol) are heated to 135° C. at 15 mm Hg. Phenol starts to distil off after a short time. The diethylene glycol is prevented from being carried off with the distillate by supplying the condenser with hot water at 90° C. The temperature is raised to 165° C. in the course of 9 hours according to the rate of distillation. 5350 g of phenol have by then been distilled off (98.5% of the theory). The temperature is then raised to 180° C. and a vacuum of 0.2 mm Hg is applied to the apparatus, the temperature of the cooling water being lowered to 60° C. A further 70 g of phenol distil off in the course of one hour. Total quantity 5420 g (100% of the theory).

A colourless viscous oil of OH number 94.8 is obtained. The aromatic content is not detectable.

EXAMPLE 5

40 Triethylene glycol polycarbonate prepared on a laboratory scale and therefore without inert gas treatment.

In a 10 l three-necked flask equipped with a stirrer, immersion thermometer and a packed fractionating column, 4725 g of triethylene glycol (31.5 mol) and 4815 g of diphenyl carbonate (22.5 mol) are heated at 140° C. at 15 mm Hg. Phenol starts to distil off after one hour. In the course of 11 hours, the temperature is raised to 200° C. according to the rate of distillation. 4180 g of phenol have by then been distilled off (99% of the theory). By brief application of a vacuum of 0.2 mm Hg, a further 40 g of phenol can be removed.

An almost colourless oil of OH number 191 was obtained. The aromatic content was as follows:

0.06% of free phenol	
<0.01% of phenol as phenyl carbonate	60
<0.01% of phenol as phenylether	

WHAT WE CLAIM IS:—

1. A process for the production of a difunctional aliphatic polycarbonate which has terminal hydroxyl groups and a molecular weight of 600 to 5,000 and a "total phenol", as herein defined, of not more than 0.15% by weight, which comprises the steps of reacting at least one dihydric alcohol and diphenylcarbonate (a) in a first reaction stage at 100 to 170° C. under reduced pressure until more than 90% of the amount of phenol which should theoretically be liberated has distilled off, (b) in a second reaction stage in which the quantitative reaction of diphenylcarbonate or of intermediate products containing phenyl carbonate groups is then completed under reduced pressure at 170 to 205° C. and if necessary (c) in a third reaction stage in which the product of the process is freed from residual phenol at 180 to 205° C. under reduced pressure.
2. A process as claimed in claim 1 in which step (c) is carried out at 0.1 to 0.5 mm Hg.
3. A process as claimed in claim 1 in which step (c) is carried out by passing a stream of inert gas through the product under reduced pressure.
4. A process as claimed in claim 3 in which the reduced pressure is 5 to 30 mm Hg.
5. A process as claimed in claim 3 or claim 4 in which the inert gas is oxygen free.
6. A process as claimed in any of claims 1 to 5 in which step (b) is carried out at a pressure of less than 15 mm Hg.
7. A process as claimed in any of claims 1 to 6 in which the dihydric alcohol is hexane-1,6-diol.
8. A process as claimed in claim 1 substantially as herein described with reference to any one of the Examples.
9. Aliphatic polycarbonates when prepared by a process as claimed in any of claims 1 to 8.
10. A polyurethane elastomer when prepared from a polycarbonate as claimed in claim 9.

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